

Miniature Sensor Probe for O₂, CO₂, and H₂O Monitoring in Portable Life Support Systems

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A miniature sensor probe, composed of four sensors which monitor the partial pressure of O₂, CO₂, H₂O, and temperature, designed to operate in the portable life support system (PLSS), has been demonstrated. The probe provides an important advantage over existing technology in that it is able to operate reliably while wet. These luminescence-based fiber optic sensors consist of an indicator chemistry immobilized in a polymeric film, whose emission lifetime undergoes a strong change upon a reversible interaction with the target gas. Each sensor includes chemistry specifically sensitive to one target parameter. All four sensors are based on indicator chemistries that include luminescent dyes from the same chemical family, and therefore exhibit similar photochemical properties, which allow performing measurements of all the sensors by a single, compact, low-power optoelectronic unit remotely connected to the sensors by an electromagnetic interference-proof optical fiber cable. For space systems, using these miniature sensor elements with remote optoelectronics provides unmatched design flexibility for measurements in highly constrained volume systems such as the PLSS. A 10 mm diameter and 15 mm length prototype multiparameter probe was designed, fabricated, tested, and demonstrated over a wide operational range of gas concentration, humidity, and temperature relevant to operation in the PLSS. The sensors were evaluated for measurement range, precision, accuracy, and response time in temperatures ranging from 50°F-150°F and relative humidity from dry to 100% RH. Operation of the sensors in water condensation conditions was demonstrated wherein the sensors not only tolerated liquid water but actually operated while wet.

DLR	=	dual lifetime referencing
dpp	=	dipyridophenazine
τ	=	emission lifetime
EMU	=	extravehicular mobility unit
EVA	=	extravehicular activity
f	=	frequency
FOCS	=	fiber optic chemical sensor
FRET	=	fluorescence resonance energy transfer
HPTS	=	1-hydroxypyrene-3,6,8-trisulfonate
ISS	=	International Space Station
LED	=	light emitting diode
MLCT	=	metal-to-ligand charge transfer
NASA	=	National Aeronautics and Space Administration
ϕ	=	phase
$p\text{CO}_2$	=	partial pressure of carbon dioxide
PDMS	=	poly(dimethylsiloxane)

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PLSS	=	Portable Life Support System
pO_2	=	partial pressure of oxygen
RH	=	relative humidity
$(Ru(dip)_3)_2$	=	<i>tris</i> (4,7-diphenyl-1,10-phenanthroline)ruthenium(II)
SBIR	=	Small Business Innovation Research
Sn-1	=	standard deviation
t_{95}	=	response time
TOA	=	tetraoctylammonium

I. Introduction

Advanced space suits require lightweight, low-power, durable sensors for monitoring critical life support components, including partial pressure of carbon dioxide (CO_2), oxygen (O_2) and water vapor (H_2O) in the Portable Life Support System (PLSS). Top-level requirements for Extra Vehicular Activity (EVA) system improvements include reduction of system size, weight, and power, non-consumption of resources, increased hardware reliability, durability, and operating life. Environmental conditions include functionality in microgravity, low pressure, elevated oxygen environments and, specifically in the PLSS, operation in moist gases. Relative humidity in a space suit typically ranges from 75% RH to 100% RH, so liquid condensation should be expected. No current compact sensors have the tolerance for liquid water that is specifically required.¹ Most existing gas sensors exhibit hysteresis after condensation, and poor accuracy near water vapor saturation. NASA requires space suit gas sensors that function reliably under these conditions.

Indicator-based fiber optic chemical sensors (FOCS) offer an excellent alternative to electrical analysis methods and to direct spectroscopy measurements when miniaturization and operation at elevated humidity is required. On luminescent indicator-based FOCS, the sensor materials consist of a luminescent indicator, whose emission properties depends on the target chemical concentration, supported in a chemically and mechanically passive polymeric matrix, which is placed at the end of an optical cable. For space systems control, miniature fiber optic sensors connected to the electronic circuitry by an optical fiber cable allow greater flexibility in placing the sensor in highly constrained volume systems such as the PLSS.

The maturity, high performance, and increasing market share reached by luminescence-based oxygen sensors are the bases of the fiber optic multiparametric probe we present herein. Optical oxygen sensors developed by IOS and others are a well proven technology that combines minimal weight, easy miniaturization, and long durability, and does not consume oxygen (unlike most electronic sensors). The commercial success and superior performance of these sensors, in comparison even to other optical chemical sensors, is based on two main features: **(1) emission lifetime-based readout, instead of intensity-based measurements.** The emission lifetime of the indicator undergoes a strong but fully reversible change upon interaction with the oxygen, without any consumption of either the indicator or the O_2 ; and **(2) compact phase-resolved luminescence detectors for emission lifetime determination.** Based on these factors and our experience, we have developed a miniature probe incorporating **sensors for O_2 , CO_2 , H_2O and temperature.** In these sensors, the emission lifetime of each specific indicator chemistry depends on the concentration of the target analyte. In contrast to emission intensity readings, measurements that rely on emission lifetime are insensitive to indicator bleaching, fluctuations in light source intensity or photodetector sensitivity, and the alignment of optical components, making them almost drift-free. A single low-power, compact, phase-resolved luminescence detection unit can be used for interrogating all three optical sensors.

We present the work conducted in the development and analytical characterization of the above mentioned sensors, and the incorporation of them into a miniature sensor probe. Commercially available phase-resolved luminescence detectors were used for the sensor interrogation in the laboratory. An electronic readout unit that would qualify for space application is under development, but is not the subject of the work presented herein.

II. Phase Resolved Luminescence Detection

Amplitude measurements (i.e., those based on the intensity of emission from the indicator) are subject to interference due to the photodecomposition or bleaching of the indicator, to fluctuations in the excitation source intensity and/or the detector response and to optics alignment.

In contrast, time domain measurements rely on the emission lifetime (a parameter characterizing the emission decay kinetics), and are therefore insensitive to these interferences, resulting in reliable, stable measurements. Time domain techniques have the additional advantage of not requiring a reference signal value to perform absolute measurements.

The direct determination of luminescence decay kinetics or emission lifetime requires complex and costly instrumentation. However, comparatively simple and compact **phase-resolved luminescence measurement** equipment that can indirectly determine the emission lifetime can be manufactured at low cost.

In phase-resolved measurements, the instrument generates a continuous wave sinusoidal waveform of a known and programmable frequency that modulates the light source illuminating the indicator contained in the probe tip. As a result, the luminescence signal from the indicator dye is intensity modulated at the same frequency as the excitation source. However, because of the finite lifetime of the dye's excited state, there is a phase delay between the excitation signal and the sensor signal (Fig. 1). An estimate of the fluorescence lifetime of the indicator probe can then be computed by comparing the phase (ϕ) information of the excitation and sensor signals ($\tan\phi = 2\pi f\tau$), where f is the modulation frequency and τ is the emission lifetime of the probe.²

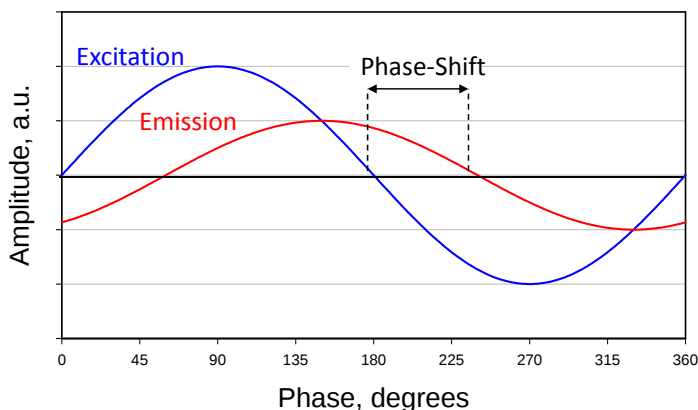


Figure 1. Excitation signal modulated in intensity, emission signal modulated at the same frequency, and phase shift resulting from the luminescence.

III. Carbon Dioxide Sensor Preparation and Characterization

The sensitive materials consist of chemistry optically sensitive to pH variation, embedded in a PDMS-based polymer. PDMSs show high gas permeability and good optical properties, and can withstand a wide range of temperatures, usually from -40°C to around 200°C , without experiencing structural changes. The diffusion of the CO_2 towards the inside of the sensor material, with subsequent hydration, generates carbonic acid. For that, water molecules have to be present in the sensor materials. The corresponding pH change is detected by monitoring the properties of the pH optical indicator. The PDMS is a gas-permeable, water-impermeable polymer, preventing interaction of the indicator with liquid water when it condenses.

We have investigated various chemistries and pH indicators that respond to the presence of CO_2 with variations in their phase shifts, including indicator chemistries based on Dual Lifetime Referencing (DLR) (for a detailed explanation of the DRL technique, see Refs. 3, and 4)) based on fluorescence resonance energy transfer (FRET) (for a detailed explanation of the FRET method, see Ref. 5) and based on Ru(II) complexes, the emission lifetimes of which are sensitive to the presence of acids.⁶

Following the DRL approach, we have used (1-hydroxypyrene-3,6,8-trisulfonate), HPTS, as the pH sensitive indicator, because of its high chemical stability, strong visible absorption band, and large Stokes shift emission band. The indicator was incorporated, as an ion pair of tetraoctylammonium, PTS(TOA)₄, into PDMS-based films. This hydrophobic ion pair is compatible with the PDMS, facilitating the indicator distribution in the polymer matrix.

IV. Sensor Characteristics

Under standard conditions (75°F and RH 50%) the sensor exhibits a measurement range from 0 to 3.0 psi $p\text{CO}_2$ (or higher), with a limit of detection of 1.5×10^{-4} psi $p\text{CO}_2$. The calibration curve in the measurement range of interest for application in PLSSs (from 0 to 0.3 psi $p\text{CO}_2$) is shown in Fig. 2. The response of the sensor is not linear with the CO_2 concentration, and therefore a linearization function has to be applied to establish the sensor out signal.

The measurement range, limit of detection, and calibration curve of the selected CO₂ sensor depend on the temperature and relative humidity. The performance of the sensor in the target matrix of environmental conditions is reported below.

The precision of the sensor was calculated as the standard deviation of several consecutive readings at different levels of $p\text{CO}_2$ (repeatability), at variable humidity levels at 75°F, and at variable temperatures at 50% RH. After sensor calibration, the accuracy was calculated as the deviation of the sensor reading from the actual value of $p\text{CO}_2$. The accuracy calculation was conducted at the standard conditions of 50% RH and 75°F, since the accuracy calculation at different environmental conditions will depend on the algorithms applied to compensate for temperature and humidity (beyond the scope of Phase I). Certified cylinders of CO₂ and nitrogen, and mass flow controllers calibrated by the manufacturer before starting the tests were used to generate the target $p\text{CO}_2$ levels.

The repeatability between readings at a constant $p\text{CO}_2$ level was excellent, as shown in Fig. 2, resulting in a sensor precision of 0.020 psi or better in the 0 to 0.3 psi range. The accuracy of the sensor was 0.009 psi or better in the 0 to 0.30 psi range, which means 3% of full scale or better.

V. Sensor Response when Exposed to Liquid Water

The CO₂ sensors now in use in the PLSS cannot operate when there is water condensation on the sensor, and must be replaced by a newly calibrated unit after being exposed to liquid water. For this reason, demonstrating operation under wet conditions was an important goal of our research.

In the tests performed to demonstrate operation under water condensation, the relative humidity was initially set at 85% and then was increased to 100%. In this condition after 10 to 20 minutes (depending on the test), water condensation is detected on the top of the sensor. The condensation of liquid water distorts the amplitude of the signal, but does not significantly affect the phase shift measurement (Fig. 3). After condensation is detected, the response of the sensor is recorded at several levels of CO₂ and then the humidity level is set again at the initial value of 85% in order to demonstrate both (1) sensor operation when wet and (2) sensor response stability after drying the liquid water.

Since the sensor response depends on the humidity, as discussed below, the signals at 100% relative humidity and when the sensor is exposed to liquid water are different from the response at 85% RH, so the sensor signal must be compensated for RH. The response of the sensor during the test is shown in Fig. 3.

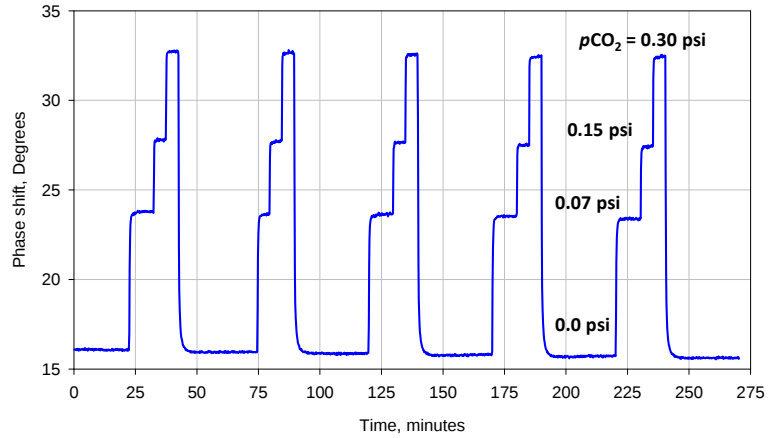


Figure 2. Response profile of a sensor exposed to varying levels of $p\text{CO}_2$ (0, 0.07, 0.15 and 0.30 psi) at 75°C and 50% RH during a test performed to determine sensor precision.

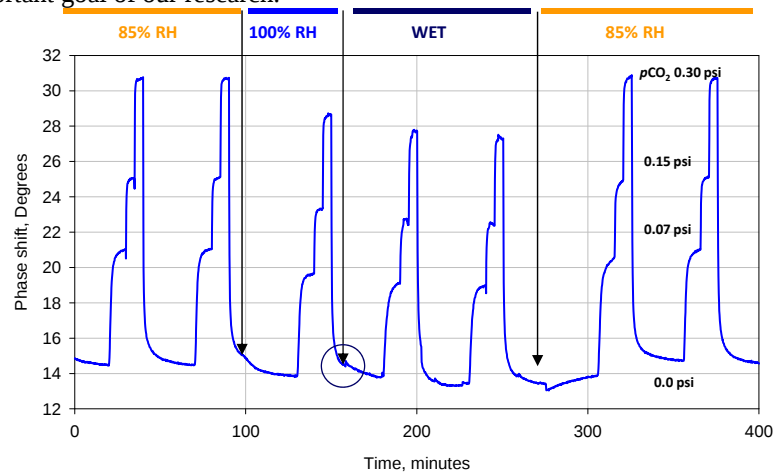


Figure 3. Response profile of a sensor exposed to variable levels of $p\text{CO}_2$ (0, 0.07, 0.15 and 0.30 psi) at 75°F and 85% RH, 100% RH and wet.

Fig. 4 shows the sensor response before and after the wet period. The films prepared with PDMS can retain water molecules inside the film, and at the same time are still hydrophobic enough to be impermeable to liquid water.

The sensor showed a very consistent and repeatable response in tests performed with over 8 hours under wet conditions.

VI. Optical Humidity Sensor

It is known that Ru(II) polypyridyls containing a dipyrrophenazine (dpp) chelating ligand are sensitive to the presence of water. Interaction of the latter with a low-lying π^* orbital of dpp decreases its energy below the emissive metal-to-ligand charge transfer (MLCT) state of the complex, and switches off its luminescence.⁷ The result is a very low emission in the presence of water, but a strong emission when water is removed, for instance when the indicator is in a non-aqueous environment like a polymer matrix.^{8,9} The surrounding polymer where the indicator dye is embedded modulates such a behavior. We prepared a sensor based on the use of a ruthenium complex incorporating dpp chelating ligand as indicator, and on phase resolved luminescence measurements.

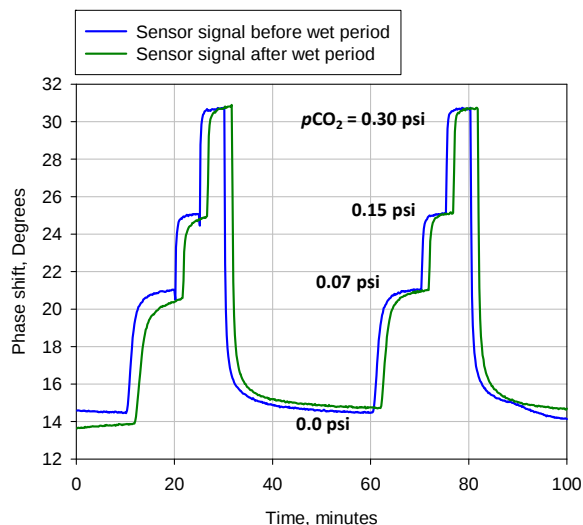


Figure 4. Response profile of a sensor exposed to varying levels of $p\text{CO}_2$ (0, 0.07, 0.15 and 0.30 psi) at 75°F and 85% RH, before and after liquid water condensation. Signals purposely offset to aid comparison.

A. Sensor Characteristics

The sensors developed showed a measurement range between 0 and 100% relative humidity (RH) under oxygen and nitrogen background, accuracy of 2% or better, response time (t_{95}) of 3 s from 0 to 98% RH, and faster for other humidity levels, precision of 0.15% RH or better (at 75°F), and minimal or no hysteresis. Operation of the sensors in the desired temperature range (50°F to 150°F) was demonstrated. A tolerance to repeated water condensation and the stability of the sensors under stress conditions (exposed to boiling water vapors for 24 h) was demonstrated. The typical response of the optical sensor to humidity is shown in Fig. 5. A Honeywell HIH4000 sensor was used during the tests as control.

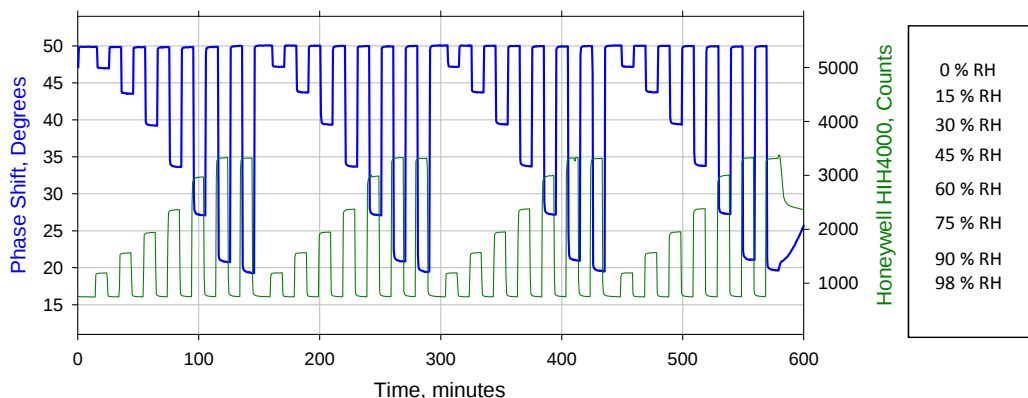


Figure 5. Blue track: Response profile of an optical humidity sensor when exposed cyclically to dry gas (phase shift = 50°) and to variable levels of humidity (0, 5, 15, 30, 60, 75, 90 and 98% RH) at 23°C. Green track: Response of a commercial RH sensor (Honeywell HIH4000).

B. Sensor Response when Exposed to Liquid Water

After calibration, the sensors were exposed cyclically to oxygen saturated with humidity until water condensation was detected, and then to a fixed value of RH equal to 32.2%. The readings of the sensors, after detecting water condensation, were recorded, and the corresponding RH values were determined from the phase shift measurements using the calibration curve previously developed. No significant deviation of the sensor response

was found after water condensation; the sensor returned to within 0.2% RH of its original reading (32.2% RH) after each condensation event (Fig. 6).

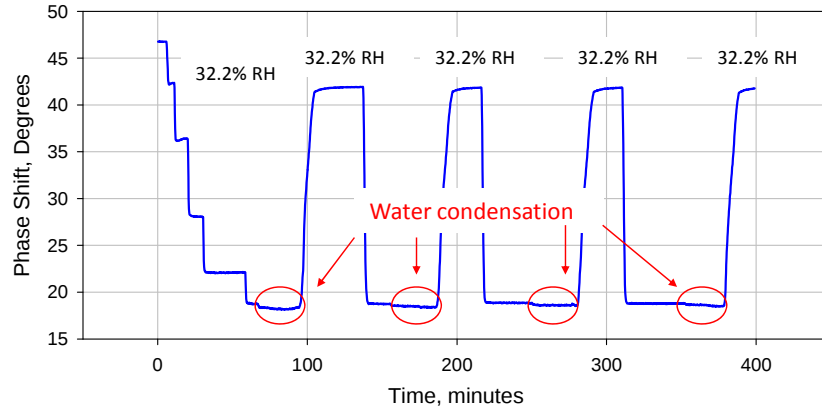


Figure 6. Response profile of a fiber optic humidity sensor when exposed at 23°C to variable levels of humidity for calibration (16.2, 32.2, 48.3, 64.5, 80.5, and 97% RH) and then to cycles of increasing humidity until observing water condensation and decreasing humidity to 32.2% RH.

VII. Optical Oxygen Sensor

Ruthenium (II) complexes have been used at IOS for oxygen sensing for more than a decade, including the ion *tris*(4,7-diphenyl-1,10-phenanthroline)ruthenium(II), $(\text{Ru}(\text{dip})_3)^{2+}$, the most common indicator in commercial optical oxygen sensors. This indicator undergoes an effective deactivation of its strong luminescence in the present of oxygen, and presents absorption and emission bands in the visible region of the spectrum and high chemical and photochemical stability. The long emission lifetime (7-8 μs) of this indicator results in high sensitivity to oxygen deactivation by collision, resulting in deep quenching and very large lifetime shifts. We prepared oxygen sensitive films by incorporating the ruthenium complex $(\text{Ru}(\text{dip})_3)^{2+}$ into PDMS-based films.

A. Sensor Characteristics

The sensors show a measurement range between 0 and 14.7 psi $p\text{O}_2$, accuracy of 0.03% at 3.1 psi, and precision of 0.04% (Sn-1, n=20) at 3.1 psi and 75°F. A typical response profile of the oxygen sensor when exposed to six levels of $p\text{O}_2$ during a 50 hour test is shown in Fig. 7.

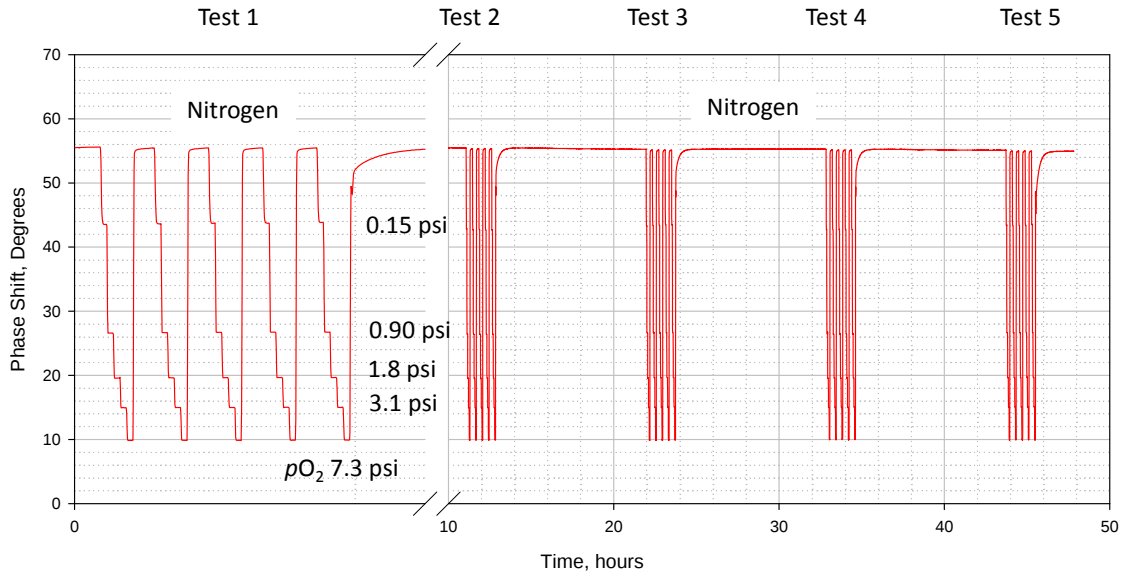


Figure 7. Example response profile of an oxygen sensitive film when exposed to six levels of $p\text{O}_2$ (0, 0.15, 0.90, 1.8, 3.1 and 7.3 psi) at 25°C, 50% RH, and 0.4 L/min.

B. Sensor Response when Exposed to Liquid Water

Humidity had none or minimal effect on sensor response (Fig. 8), and operation while wet was demonstrated.

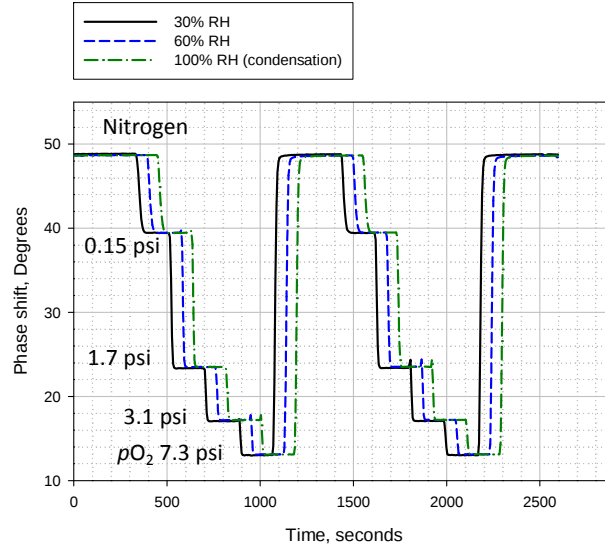


Figure 8. Response profile of an oxygen sensitive film when exposed to five levels of pO_2 (0, 0.15, 1.7, 3.1 and 7.3 psi) at 18°C, and 30% RH, 60% RH, and 100% RH. Signals purposely offset to aid comparison.

VIII. Temperature Sensor

A novel optical sensor for temperature was developed. Having a temperature sensor integrated into the multiparametric probe, near the gas sensors, would improve the accuracy of the temperature compensation in the oxygen, humidity, and carbon dioxide sensors. In addition, by incorporating an optical rather than electrical temperature sensor we can connect the readout unit with the sensor probe via an electromagnetic interference (EMI)-proof optical fiber cable. The final selection of the temperature sensor to be used for correcting the H_2O , O_2 , and CO_2 sensor signal will depend on the desired interface with the PLSS.

The temperature sensor was fabricated by depositing a luminescent Ru(II) organometallic dye in a polymeric film. The doped film was then encapsulated between a thin metal film and an optical window. In that way, the film is not exposed to the gases and only the temperature can affect the emission lifetime of the dye.¹⁰

The sensor response in the target temperature range is shown in Fig. 9. The sensor exhibited excellent repeatability and sensitivity in the target temperature range.

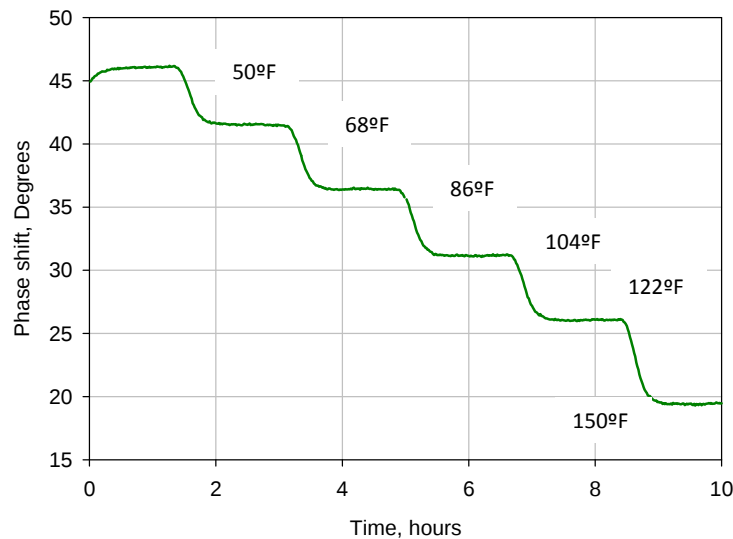


Figure 9. Response profile of the novel luminescence sensor for temperature in the range of 50°F to 150°F.

IX. Sensor Probe Design and Fabrication

A first design of the sensor probe (including the optical cable) was performed, and a first prototype was produced. The objective was to demonstrate a sensor probe 10 mm in diameter, and validate the performance of the sensors incorporated in the probe.

The probe consists of four sensors incorporated in a single body 10 mm in diameter at the distal part of a package of fiber optic cables. Each individual sensor cable consists of a fiber optic 1:2 bifurcated bundle and a cup with incorporated film of the sensing material. The design of the distal part makes it easy to replace the sensing material in the cup (for development purposes). The split bundles were fabricated from high OH synthetic silica optical fibers with only 0.01-0.012 dB/m attenuation in the spectral region of interest (red). These types of fiber also have high transmission in the visible (around 470 nm) spectral region. One of the two legs of each bifurcated bundle is attached to the LED interrogation light source, and the second is attached to the photodetector of the phase-resolved luminescence detector. The optical fibers in the common leg of the bifurcated bundle are randomized and fabricated with a high packing density. The packing factor of each individual cable is approximately 60%-63% because of the cladding and the resin that holds the optical fibers together. The design of the probe and pictures of the prototype are shown in Fig. 10.

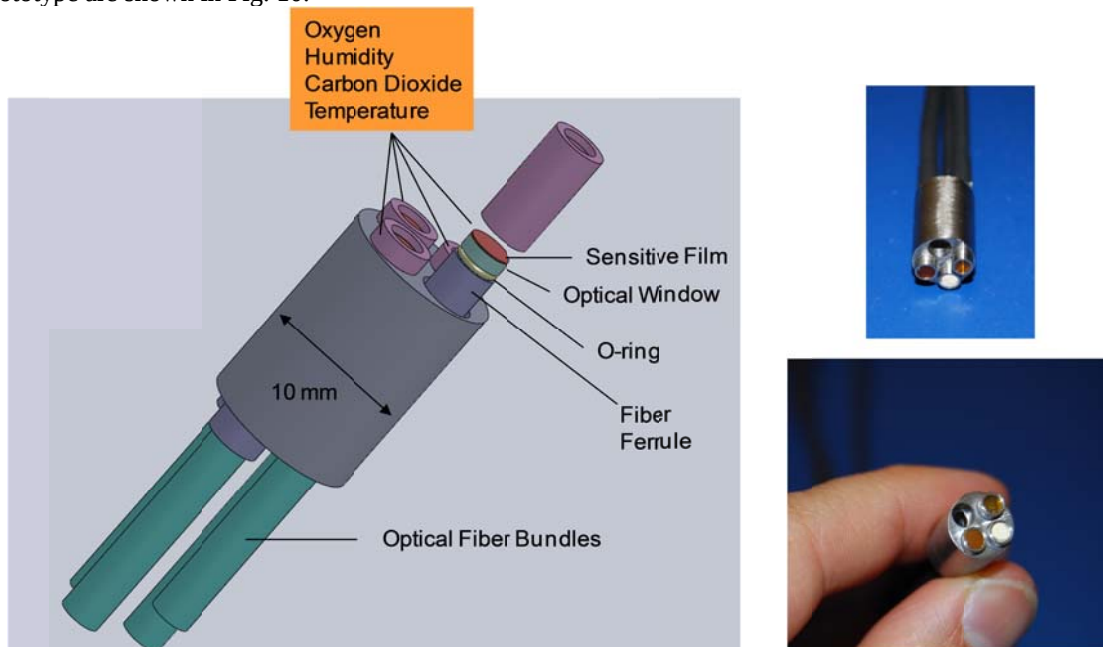


Figure 10. (Left) Design of the fiber optic multiparametric probe. (Right) Probe prototype, incorporating sensor films for oxygen, humidity, and carbon dioxide.

X. Sensor Probe Validation

To validate the multisensory probe for operation in the PLSS, we tested the four-sensor prototype at variable humidity levels from dry to 100% RH, and variable temperature from 50 to 150°F. The operation of the sensor probe over the desired range on temperature and humidity was demonstrated (Fig. 11, 12 and 13), and temperature correction will be applied for the oxygen and humidity sensors. For the CO₂ sensor, correction for both temperature and humidity will be needed.

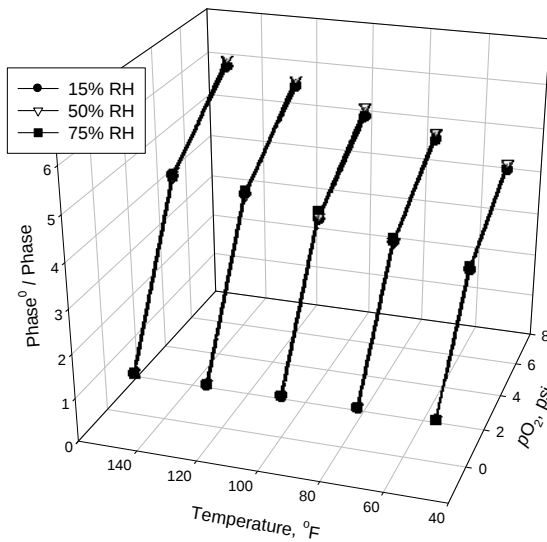


Figure 11. Response profile of the novel luminescence sensor for temperature in the range of 50°F to 150°F.

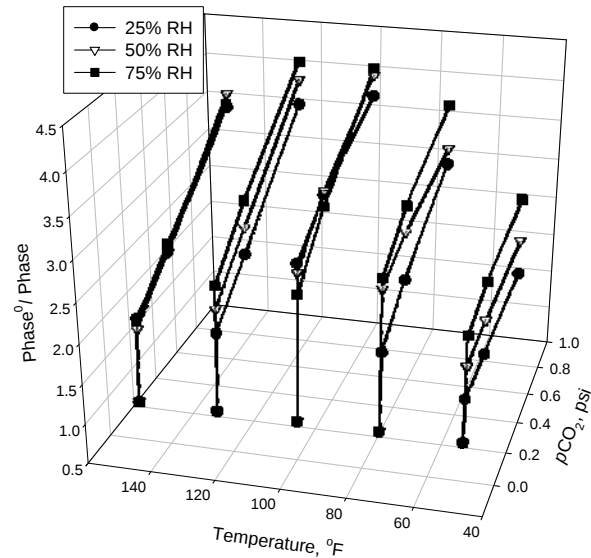


Figure 12. Calibration curves for the CO₂ sensors at three relative humidity levels and five temperatures. Phase shift⁰: phase shift in nitrogen.

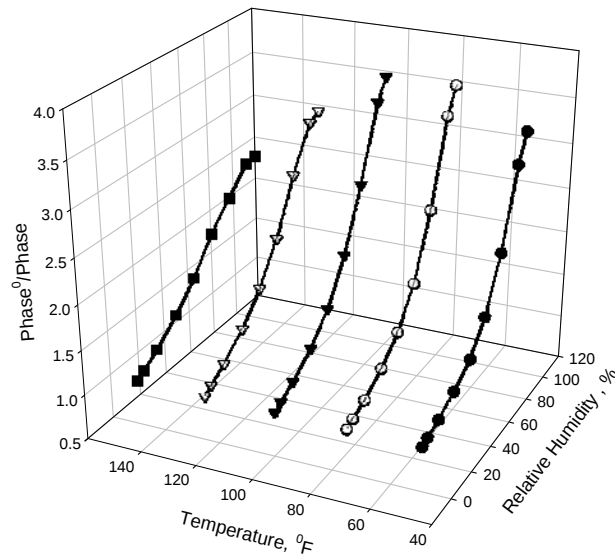


Figure 13. Calibration curves for the H₂O sensor at five temperatures. Phase shift⁰: phase shift in dry nitrogen.

XI. Conclusion

The overall goal of the work presented was to demonstrate the feasibility of an optical flow-through monitor for partial pressure of O₂, CO₂, H₂O and temperature in PLSS, capable of operating under conditions of liquid water condensation in space, and in the temperature range of 50°F-150°F.

Three approaches were evaluated for preparing CO₂ sensors based on emission lifetime measurements, and DLR-based sensor were selected for their incorporation in the miniature probe. As part of the CO₂ sensor evaluation and testing, we performed tests to evaluate the measurement range of the sensors, precision and accuracy of the sensors, and response time and response curve of the sensors in a 50°F-150°F temperature range. The sensor operation under conditions of liquid water condensation was demonstrated. Sensors for oxygen, humidity, and temperature monitoring were also prepared and tested, based on ruthenium (II) complexes and phase-resolved

luminescence measurements. A 10 mm diameter by 15 mm length prototype multiparameter probe was designed and fabricated, including the four fiber optic sensors. The operation of the multiparameter probe over a realistic range of humidity and temperature was demonstrated.

The project directly addresses a NASA need for advanced space suit sensing technologies, including the current ISS EMU and the new EMU development.

Acknowledgments

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References

- ¹ Lu, S.- D., Lin, A., Campbell, M., Smith, F., and Curley, S., "Development of a Test Facility for Air Revitalization Technology Evaluation," NASA 07ICES-295, 2007.
- ² Holst, G. A., Kühl, M., Klimant, I., and Scheggi, A. V., "Novel Measuring System for Oxygen Micro-optodes Based on a Phase Modulation Technique," *Proceedings of SPIE - The International Society for Optical Engineering*, Vol. 2508, 1995, pp. 387-398.
- ³ Mayr, T., Klimant, I., Wolfbeis, O. S., and Werner, T., "Dual Lifetime Referenced Optical Sensor Membrane for the Determination of Copper(II) Ions," *Analytica Chimica Acta*, Vol. 462, No. 1, 2002, pp. 1-10.
- ⁴ Cajlakovic, M., Bizzarri, A., and Ribitsch, V., "Luminescence Lifetime-Based Carbon Dioxide Optical Sensor for Clinical Applications," *Analytica Chimica Acta*, Vol. 573-574, 2006, pp. 57-64.
- ⁵ Lakowicz, J. R., *Principles of Fluorescence Spectroscopy*, 2nd ed., Kluwer/Plenum, New York, 1999.
- ⁶ Orellana, G., Morino-Bondi, N. C., Segovia, B., and Marazuela, M. D., "Fibre-Optic Sensing of Carbon Dioxide Based on Excited-State Proton Transfer to a Luminescent Ruthenium(II) Complex," *Analytical Chemistry*, Vol. 64, No. 19, 1992, pp. 2210-2215.
- ⁷ Zhou, Q., Shahriari, M. R., Kritz, D., and Sigel, G. H., "Porous Fiber-Optic Sensor for High-Sensitivity Humidity Measurements," *Analytical Chemistry*, Vol. 60, No. 20, 1998, pp. 2317-2320.
- ⁸ Bedoya, M., Diez, M. T., Moreno-Bondi, M. C., and Orellana, G., "Humidity Sensing with a Luminescent Ru(II) Complex and Phase-sensitive Detection," *Sensors and Actuators B*, Vol. 113, No. 2, 2006, pp. 573-581.
- ⁹ Papkovsky, D. B., Ponomarev, G. V., Chernov, S. F., Ovchinnikov, A. N., Kurochkin, I. N., "Luminescence Lifetime-based Sensor for Relative Air Humidity," *Sensors and Actuators B*, Vol. 22, No. 1, 1994, pp. 57-61.
- ¹⁰ Filevich O., and Etchen, R., "1D and 2D Temperature Imaging with a Fluorescent Ruthenium Complex," *Analytical Chemistry*, Vol. 78, No. 21, 2006, pp. 7499-7503.